New type of excitatory pulse coupling of chemical oscillators via inhibitor

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Electronic Supplementary Information (ESI)

ESI consists of: (1) two photographs of the setup used, (2) Table 1 for reactions and constants of the model: eqs. (1) – (4) that describe the mechanism of the Belousov-Zhabotinsky reaction, (3) figures that provide more details about the results of simulations.

(1) Two photographs of the setup the scheme of which is shown in Fig. 2.

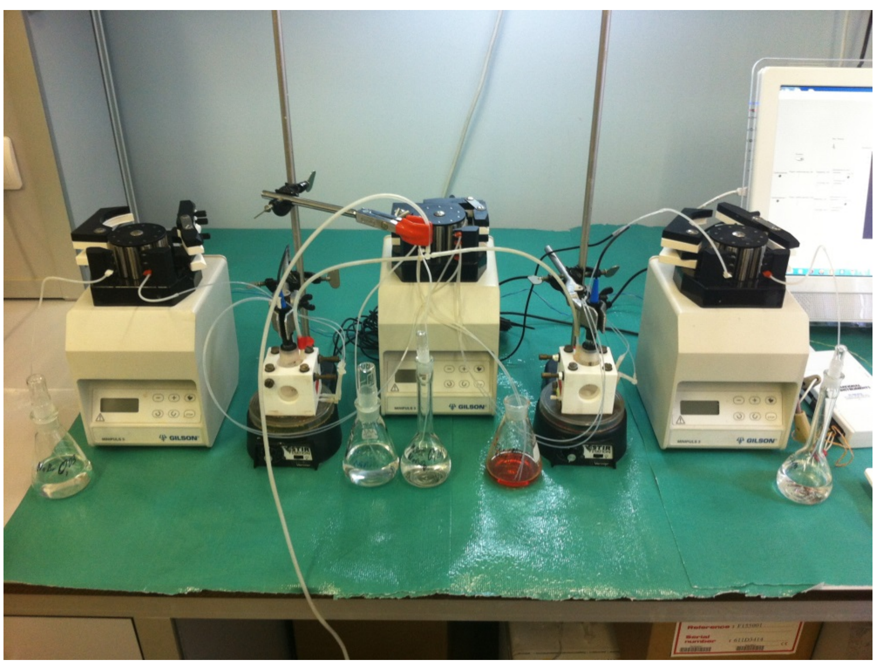

Fig. S1. Teflon reactors, Pt-electrodes, magnetic stirrers, peristaltic pumps, reservoirs with reactants.

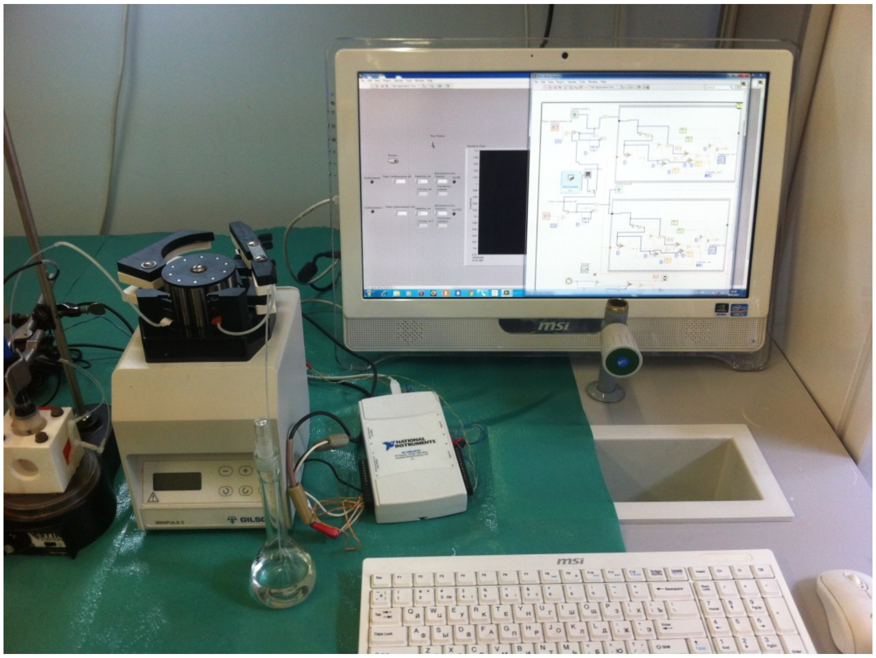

Fig. S2. Scheme of a LabVIEW program developed by us (at the screen of the PC), DAQ National Instruments.

(2) Table 1 for the reactions and constants of model (1) – (4).

Term $k_1(h)xy$: Annihilation of activator X and inhibitor Y and production of BrMA (= V).	$X + Y \rightarrow 2V$ $HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$ $2HOBr + MA \rightarrow BrMA + H_2O$	$k_1(h) = k_1'h$, $k_1' = 2 \times 10^6\ M^{-2}s^{-1}$
Term $k_2(h)y$: Slow emergence of X and slow production of BrMA.	$Y \rightarrow X + V$ $Br^- + BrO_3^- + 2H^+ \rightarrow HBrO_2 + HOBr$ $HOBr + MA \rightarrow BrMA + H_2O$	$k_2(h) = k_2'h^2A$, $k_2' = 2\ M^{-3}s^{-1}$
Term k_3x^2: Disproportionation of X and production of BrMA	$X + X \rightarrow V$ $HBrO_2 + HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$ $HOBr + MA \rightarrow BrMA + H_2O$	$k_3 = 3000\ M^{-1}s^{-1}$,
Term $k_4(h)x(c_0 - z)/(c_0 - z + c_{min})$: Autocatalysis with the restriction term $(c_0 - z)/(c_0 - z + c_{min})$ that stops autocatalysis if c (= c_0 - z) is close to c_0.	$X \rightarrow 2X + 2Z$ $HBrO_2 + BrO_3^- + H^+ \rightarrow 2BrO_2^\bullet$ $2BrO_2^\bullet + 2C \rightarrow HBrO_2 + 2Z$	$k_4(h) = k_4'hA$, $k_4' = 42\ M^{-2}s^{-1}$, $c_{min} = (3k_rk_{10}c_0)^{1/2}/k_{red}$, $k_r = 2 \times 10^8\ M^{-1}s^{-1}$, $k_{10} = k_{10}'[MA]$, $k_{10}' = 0.05\ M^{-1}s^{-1}$, $k_{red} = 5 \times 10^6\ M^{-1}s^{-1}$
Term k_9vz: Production of Y from BrMA	$V + Z \rightarrow Y$ BrMA + ferriin $\rightarrow$ Br^- + products	$k_9 = 20\ M^{-1}s^{-1}$
Term $k_{10}z$: Reduction of ferriin in reaction with MA	$Z \rightarrow 0$ ferriin + MA $\rightarrow$ ferroin + products	$k_{10} = k_{10}'[MA]$, $k_{10}' = 0.05\ M^{-1}s^{-1}$
Term $k_{13}v$: All reactions that lead to a consumption of BrMA	$V \rightarrow 0$ BrMA $\rightarrow$ products BrMA + ferriin $\rightarrow$ products	$k_{13} = 0.004\ s^{-1}$

Z = ferriin, C = ferroin, A = BrO_3^-, h = $[H^+]$, X = $HBrO_2$, Y = Br^-, V = BrMA, MA = malonic acid.

(3) Theoretical Figures

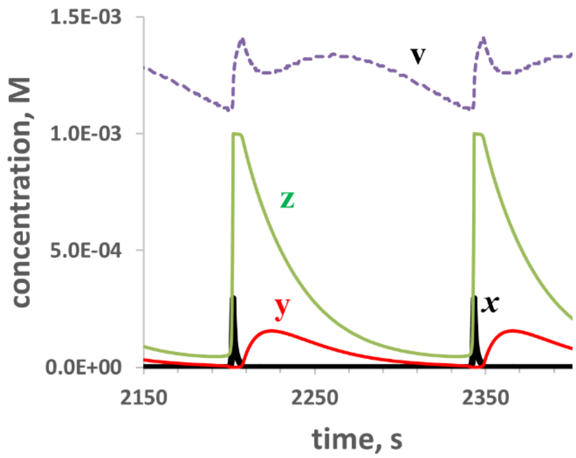

Fig. S3. Typical kinetics for equations (1) – (4) for the *i*-th oscillator without coupling:

$$\dot{x}_i = -k_1(h)x_iy_i + k_2(h)y_i - 2k_3x_i^2 + k_4(h)x_i(c_0 - z_i)/(c_0 - z_i + c_{\min}) - k_0x_i$$
$$\dot{y}_i = -k_1(h)x_iy_i - k_2(h)y_i + k_9v_iz_i - k_0(y_i - y_{i0})$$
$$\dot{z}_i = 2k_4(h)x_i\ (c_0 - z_i)/(c_0 - z_i + c_{\min}) - k_9v_iz_i - k_{10}z_i$$
$$\dot{v}_i = 2k_1(h)x_iy_i + k_2(h)y_i + k_3x_i^2 - k_9v_iz_i - k_{13}v_i - k_0v_i$$

at $h = [H^+] = 0.305$ M, A = $[BrO_3^-] = 0.25$ M, [MA] = 0.1 M, $c_0 = 10^{-3}$ M, $k_0 = 5 \times 10^{-4}$ s^{-1}, $y_0 = 0$; c_0 = [ferroin] + [ferriin], MA = malonic acid; $x = [HBrO_2]$, $y = [Br^-]$, z = [ferriin], v = [BrMA].

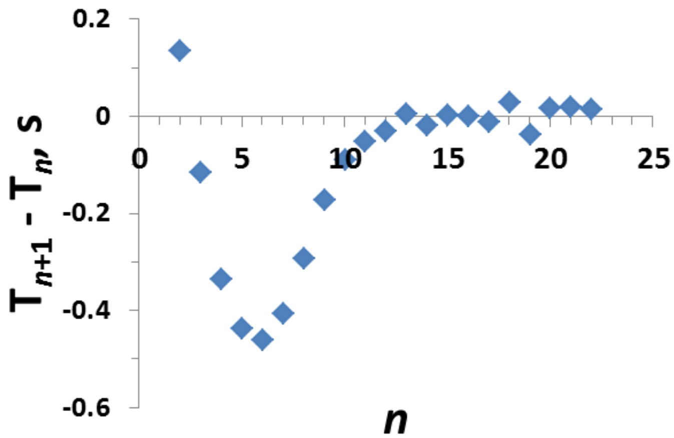

Fig. S4. The dependence of $T^{(n+1)} - T^{(n)}$ on the numbering n of perturbation in case of PRC computer experiment (presented in Fig. 4b) at τ = 42 s [region (*ii*) in Fig. 4b]. Parameters: A = 0.3 M, $h_1 = 0.5$ M, [MA] = 0.2 M, $c_0 = 1$ mM, $k_0 = 5 \times 10^{-4}$ s^{-1}, $k_B = 5 \times 10^{-5}$ s^{-1}, $y_s = 3 \times 10^{-2}$ M; $T_0 = 66$ s; $\Delta t = 5$ s.

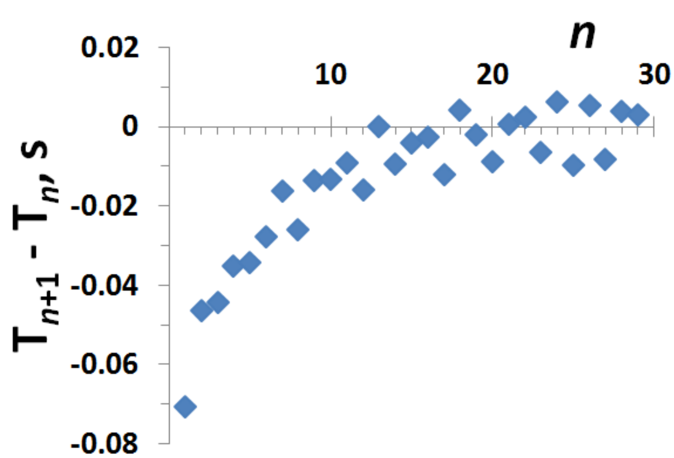

Fig. S5. The dependence of $T^{(n+1)} - T^{(n)}$ on the numbering n of perturbation in case of PRC computer experiment (presented in Fig. 4b) at τ = 2 s [region (*i*) in Fig. 4b]. All other parameters as in Fig. S4.

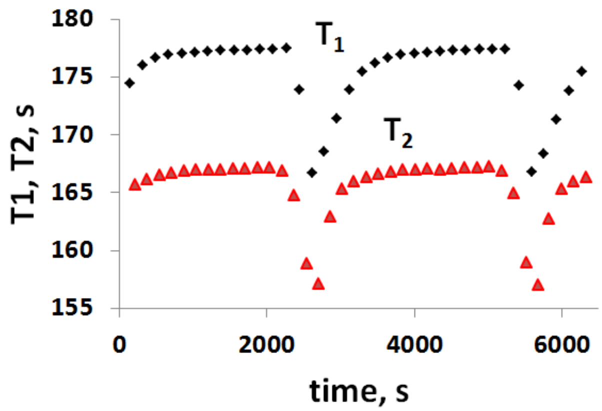

Fig. S6. The dependences of the periods T_1 and T_2 for two pulse coupled BZ oscillators on time in case of complex synchronization. Parameters: $h_1 = 0.3$ M ($T_1 = 177$ s), $h_2 = 0.31$ M ($T_2 = 167$ s), $T_2/T_1 = 0.943$, A = 0.25 M, [MA] = 0.1 M, $c_0 = 1$ mM, $k_0 = 5 \times 10^{-4}$ s^{-1}, $k_B = 7 \times 10^{-5}$ s^{-1}, $y_{s1} = y_{s2} = 5$ mM, $\Delta t = 5$ s, $\tau = 65$ s. It is seen that periods T_1 and T_2 (which is time intervals between neighboring spikes of the same oscillator) are different and change with time.